

PATENT SPECIFICATION

(11) 1222 133

1222 133

NO DRAWINGS

- (21) Application No. 25095/68 (22) Filed 25 May 1968
 (23) Complete Specification filed 22 May 1969
 (45) Complete Specification published 10 Feb. 1971
 (51) International Classification C 23 f 11/14
 (52) Index at acceptance
 C7E 12B 3
 C4X 1
 C5D 6A5D2 6B12B1 6B12B2 6B12F1 6B12FX 6B12G2A
 6B12K2 6B12N3 6B3 6C8
 CSW 5D



(72) Inventors ANGUS JOHN DUKE and ALAN FRANCIS POPPLEWELL

(54) INHIBITION OF CORROSION OF COPPER AND ITS ALLOYS USING 3-AMINO-1:2:4-TRIAZOLE

(71) We GEIGY (U.K.) LIMITED, a British Company, whose Registered Office address is Simonsway, Manchester, 22, Lancashire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to processes of inhibiting the corrosion of metals particularly of copper, or alloys containing copper, in aqueous media.

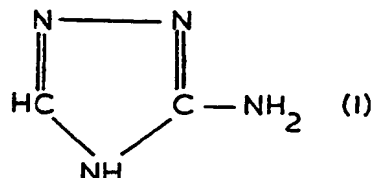
It is well known that surfaces of copper or of alloys containing copper are susceptible to corrosion and staining or tarnishing in aqueous media. Furthermore, copper corrosion products may catalyse decomposition of organic media in contact with the tarnished copper surface and may also induce corrosion of metals such as aluminium or iron.

Methods of inhibiting the corrosion of copper surfaces may be broadly classified under two headings. The first heading relates to methods in which the copper surface is subjected to a single application of inhibitor, for instance by dipping into a solution containing inhibitor or by applying a polish comprising an inhibitor. On the other hand, there are methods in which the copper surface remains in contact with a medium containing a reservoir of inhibitor, for example in the case of anti-freeze applications, or when a copper surface is contacted with a detergent composition containing a suitable inhibitor.

It is an object of the present invention to provide processes for inhibiting such corrosion of copper or copper alloy surfaces which processes fall within each of the aforementioned headings.

According to the present invention, there is provided a method of inhibiting the tarnishing

of copper or alloy of copper comprising contacting the surface of the copper or alloy thereof with a solution containing 3 - amino-1:2:4 - triazole having the formula:—



Although the method of treating a surface of copper according to the present invention may be effected using any suitable solvent for the compound of formula I, it is advantageous for most purposes to employ water as the sole solvent or as the major component of the solvent system employed. In certain applications the use in the solvent system employed of a proportion of a solvent more volatile than water is beneficial, for example, in polish compositions wherein the polish composition is to be allowed to evaporate from the treated surface. For such applications the use of solvent systems consisting of mixtures of water with water-miscible, volatile solvents such as acetone or iso-propanol is advantageous.

The proportion of the compound of formula I in the solution employed in the method according to the present invention, may vary according to the mode of application of the solution to the copper or copper alloy surface. It is preferred to use, however, in most applications a proportion of the compound of formula I within the range of from 0.005% to 5.0% by weight, a proportion within the range of from 0.05% to 2.0% by weight being particularly preferred.

There are various means by which the

[Price -

method of the present invention may be put into effect, the choice depending mainly on the physical form of the copper article to be treated and also on the nature of the desired treatment.

For instance, decorative articles, of copper or of copper alloys may be polished and a lasting tarnish resistance imparted thereto, by polishing the article in conventional manner with a polish having an aqueous or substantially aqueous base and containing a compound of formula I.

If the polish base comprises a mixture of water and alcohol, for instance iso-propanol, it may contain if desired, an abrasive such as α -alumina, red iron oxide or silica, preferably in a finely-divided form for instance in such a state of subdivision that at least 90% by weight of the abrasive material will pass through a 325-mesh (B.S.S.) sieve. Such polishes are normally allowed to dry on the polished surface and the dried film removed subsequently by light dusting.

An alternative form of metal polish contains water as the sole solvent and normally contains, in addition to abrasive materials, one or more anionic or non-ionic surface-active agents. The proportion of surface-active agent is normally and preferably within the range of from 5% to 30% by weight. In order to assist in stabilising such aqueous polish pastes, a proportion of gelling agent within the range of from 0.5% to 5% by weight is preferably present. Suitable anionic surface-active agents for use in such pastes include, for example, alkanolamine or alkali metal salts of higher fatty acids such as triethanolamine- or sodium stearate, or lauryl sulphate or sodium dodecyl benzene sulphonate. Suitable non-ionic surface-active agents include, for instance, the condensation products of ethylene oxide with alkyl phenols, higher fatty acids or higher fatty amines such as the condensation products of nine molar proportions of ethylene oxide with one molar proportion of nonyl phenol, stearic acid or hexadecylamine respectively. The gelling agent which may be present may be, for instance, methyl cellulose or polyvinyl pyrrolidone having a molecular weight in the region of 40,000.

In order to impart lasting tarnish-resistance to small, non-decorative articles of copper or copper alloy which do not require polishing, it is usually most convenient to apply the solution of the compound of formula I by a simple dipping technique. In this technique, however, it is preferred that the copper article is not maintained immersed in the solution for an unduly long time, that is a period longer than five minutes. After immersion, the treated copper article is advantageously rinsed well in water and dried using, for instance, a stream of warm air.

Another important application in which the method of treatment of the present invention

is valuable relates to the inhibition of staining of cutlery consisting of copper alloy during the washing of such cutlery with detergent compositions and during any subsequent drying operations. Such detergent compositions conventionally contain sequestering agents for calcium and other polyvalent metal ions, in order that these metal ions will not be precipitated from solution during the cleaning operation. Alkali metal poly-phosphates are often employed as the said sequestering agent, examples of such poly-phosphates being tetrasodium pyrophosphate, pentasodium tri-poly-phosphate and disodium dihydrogen pyrophosphate, penta-potassium tripoly-phosphate, sodium and potassium metaphosphate as well as commercially available mixed salts such as "hexasodium tetraphosphate" and "hexasodium hexametaphosphate".

In addition to the sequestering agent and the compound of formula I, the detergent composition may advantageously contain a surface-active agent. While the surface-active agent may be, if desired, a non-ionic surface-active agent such as a polyalkylene glycol derivative of a long-chain fatty amine, or a cationic surface-active agent such as an alkyl pyridinium halide, for instance cetyl pyridinium bromide, it is preferred to employ an anionic surface-active agent. Examples of preferred anionic surface-active agents include compounds of the formula:—



II

wherein R represents an aliphatic hydrocarbon group and M represents an alkali metal or ammonium radical. The compound of formula II may be, for instance, sodium myristyl sulphate, sodium hexadecyl sulphate, potassium stearyl sulphate, ammonium oleyl sulphate, sodium lauryl sulphate, potassium lauryl sulphate, ammonium or sodium stearyl sulphate and sodium oleyl sulphate. Other preferred classes of anionic surface-active agents include, for example, alkali metal alkyl benzene sulphonates, such as sodium dodecyl benzene sulphonate and sodium dodecyl naphthalene sulphonate; alkali metal salts of secondary alkyl sulphates such as the sodium and potassium salts of 2-ethylhexyl sulphate; and alkali metal and ammonium salts of alcohol sulphates such as the sodium, potassium and ammonium salts of lauryl alcohol sulphate.

The surface-active agent is preferably present in the detergent composition in a proportion of up to 40% by weight based on the total weight of the composition; more preferably, however, the surface-active agent is present in a proportion within the range of from 10% to 30% by weight based on the total weight of the composition.

A further application in which the method of the present invention is valuable is in the

field of acid cleaners for copper surfaces, which cleaners aid the rapid removal of tarnish from the copper surface and at the same time impart a tarnish-resisting finish to the cleaned surface.

When conventional copper tarnish inhibitors are incorporated into acidic cleaning compositions known for use in cleaning copper, the oxide-tarnish removing properties of the acidic cleaning composition are often lost, possibly because the inhibitor forms a protective layer on the oxide film; consequently removal of the oxide film is inhibited.

Unexpectedly, however, we have found that application to a copper or copper alloy surface of a composition comprising an acidic material having a pK value of not more than 5.0, thiourea and the compound of formula I, quickly removes oxide tarnish from the treated surface, and, moreover, imparts simultaneously a lasting corrosion-resistant finish to the treated surface.

Accordingly, the present invention provides as a further embodiment, a method of contacting a surface of copper or copper alloy with a solution of an acidic cleaning composition comprising an acidic material having a pK value of not more than 5.0, thiourea and the compound of formula I.

The present invention also embraces the acidic cleaning composition comprising an acidic material having a pK value not more than 5.0, thiourea and the compound of formula I. The acidic cleaning composition may be, for instance, in the form of a dry solid mixture or in the form of a solution in a suitable solvent, particularly water.

The method of treating the copper or copper alloy surface may be advantageously effected using a solution of the acidic cleaning composition according to any of a number of different techniques. For instance, the acidic cleaning composition, in the form of a dry powder may be dissolved in a suitable solvent, preferably water, to give the desired concentration of each of the individual components of the acidic cleaning composition and the copper surface may then be cleaned by immersion in this solution and have imparted thereto a tarnish resistance.

Alternatively, the acidic cleaning composition may be applied directly to the copper surface in the form of a paste, for instance, in those cases wherein it is desired to effect some polishing action, as an aqueous paste containing a mild abrasive material. Furthermore, if it is desired to employ a paste which will dry on to the surface after application in order to allow subsequent removal by dusting or rubbing, the paste advantageously contains a proportion of a water-miscible solvent, for instance, an aliphatic alcohol such as ethanol or iso-propanol.

As a further alternative, the acidic clean-

ing composition may be incorporated into an inert carrier, for instance, a dry, high wet-strength paper carrier, which after moistening with a suitable solvent, especially water, may be employed to treat the copper or copper alloy surface.

With respect to the method of copper treatment involving immersing the surface in a solution of the acidic cleaning composition, this technique is advantageously effected at an elevated temperature, for instance, a temperature within the range of from 40° C. to the boiling point of the solution, more preferably within the range of from 40° to 70° C. The proportion of thiourea in the acidic cleaning solution may be, for instance, within the range of from 0.1% to 10% by weight based on the total volume of the solution. The acidic material may be present in the acidic cleaning solution for example, in a proportion within the range of from 0.1% to 25% by weight based on the total volume of the solution. The third essential component of the acidic cleaning composition, namely the compound of formula I, may be present in a proportion within the range of, for instance, from 0.1% to 10% by weight based on the total volume of the solution.

The period during which the copper surface may be immersed in the solution of the acidic cleaning composition depends largely on such factors as the initial degree of tarnishing of the copper surface and the temperature of the solution. However, an immersion time within the range of from 30 seconds to 5 minutes is adequate for most purposes.

If the acidic cleaning composition is applied to the copper surface as a paste, for example, an aqueous paste or an aqueous alcoholic paste, the proportion of thiourea in such a paste may be, for instance, within the range of from 5% to 25% by weight based on the total weight of the paste. With regard to the acidic material, this component may be employed, for example, in a proportion within the range of from 20% to 75% by weight based on the total weight of the paste. The third essential component of the paste, namely the 3 - amino - 1:2:4 - triazole is desirably employed in a proportion within the range of from 10% to 40% by weight based on the total weight of the paste.

In addition to the three essential components described hereinbefore, the acidic cleaning composition, when employed according to the solution immersion or the paste application technique, preferably also contains a surface-active agent. Although the surface-active agent may be, if desired, a non-ionic surface-active agent, such as polyalkylene glycol derivatives of long-chain fatty amines, or a cationic surface-active agent, for instance, an alkyl pyridinium halide such as cetyl pyridinium bromide, it is preferred to employ an

anionic surface-active agent. Examples of preferred anionic surface-active agents include compounds having the formula:—



II

- 5 wherein R represents an aliphatic hydrocarbon group and M represents an alkali metal or ammonium radical. The compound of formula II may be, for example, sodium myristyl sulphate, sodium hexadecyl sulphate, potassium stearyl sulphate, ammonium oleyl sulphate, sodium lauryl sulphate, potassium lauryl sulphate, ammonium or sodium stearyl sulphate and sodium oleyl sulphate. Other preferred classes of anionic surface-active agents include, 15 for example, alkali metal alkyl benzene sulphates such as sodium dodecyl benzene sulphate and sodium dodecyl naphthalene sulphate; alkali metal salts of secondary alkyl sulphates such as the sodium and potassium salts of 2 - ethylhexyl sulphate; and alkali 20 metal and ammonium salts of alcohol sulphates such as the sodium, potassium and ammonium salts of lauryl alcohol sulphate.

- 25 The surface-active agents are preferably present in the acidic cleaning composition in a proportion of up to 40% by weight based on the total weight of the composition. More preferably, however, the surface-active agent is present in a proportion within the range 30 of from 0.1% to 10% by weight based on the total weight of the composition.

- Concerning the technique by which the acidic cleaning composition may be applied as a dry powder to an inert carrier, the carrier subsequently being moistened before application to the copper surface, the proportions of the respective components of the powder 35 may be, for example, within the following ranges:—

- | | | |
|----|--------------------------------|----------------------|
| 40 | Thiourea | 5% to 25% by weight |
| | Acidic material | 20% to 85% by weight |
| | 3 - amino - 1:2:4-
triazole | 10% to 30% by weight |

- 45 each proportion being based on the total weight of the dry composition.

A fourth application in which the method of the present invention may be put to useful effect lies in the field of anti-freeze formulations.

- 50 It is well known that an aqueous medium containing ethylene glycol, commonly employed in anti-freeze formulations, is more corrosive than is water itself towards certain metals or alloys including copper and copper alloys used in the construction of water distribution systems, especially when such metals or alloys are present in juxtaposition.

- 55 We have found that by applying the method of the present invention to anti-freeze formulations in contact with copper surfaces, pro-

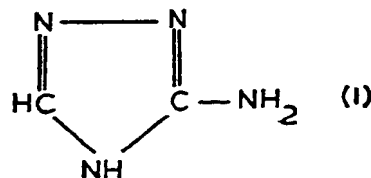
blems associated with corrosion of the copper surfaces and other metal surfaces are greatly alleviated. For instance, copper corrosion products may catalyse decomposition of inorganic media in contact with the tarnished copper surface and may also induce corrosion of metals such as aluminium or iron in contact with organic media. 65

The aqueous anti-freeze base formulation normally contains a water-miscible organic solvent, for instance, an aliphatic alcohol such as methanol or ethanol, an alkylene glycol such as ethylene glycol or glycerol. The proportion of the organic solvent in the anti-freeze base formulation is naturally dependent on climatic conditions, although an organic solvent to water ratio within the range of from 0.1:1.0 to 0.7:1.0 by weight is normally sufficient for most purposes. 70 75

The proportion of the compound of formula I in the anti-freeze base formulation may be, for example, within the range of from 0.01% to 5% by weight based on the total weight of the anti-freeze composition. 80

If desired, one or more additional corrosion inhibitors may be employed in the anti-freeze composition, for instance, benzotriazole, sodium nitrite, sodium nitrate, sodium silicate, sodium benzoate, triethanolamine phosphate, the sodium salt of 2 - mercaptobenzthiazole, and metal phosphates, arsenates, arsenites, molybdates, and/or chromates. 85 90

The present invention further provides a composition for treating a copper or a copper alloy surface comprising an aqueous carrier and 3 - amino - 1:2:4 - triazole having the formula:— 95



The aqueous carrier employed in the composition of the present invention may be, for example, water, aqueous alcohol, particularly an aqueous alcoholic polish base or other aqueous polish base, an aqueous detergent base, and aqueous acidic cleaner or an aqueous anti-freeze base particularly an aqueous ethylene glycol anti-freeze base. 100 105

The following Examples further illustrate the present invention. Parts by weight expressed therein bear the same relation to parts by volume as do kilograms to litres. 110

EXAMPLE 1

The following anti-freeze formulation (Formulation A) was made up:—

- | | |
|---|-----|
| 92.4 parts by weight of ethylene glycol | 115 |
| 2.9 parts by weight of triethanolamine | |

1.1 parts of syrupy phosphoric acid
(88—90% weight/weight H_3PO_4)
3.0 parts of borax decahydrate

of 3 - amino - 1:2:4 - triazole.

The two formulations were then tested under the Ford Motor Company Glassware Corrosion Inhibition Test (Reference No. MB—BL1—1).

- 5 An anti-freeze composition (Formulation B) was made up which was similar to Formulation A but also contained 0.6 part by weight

The weight loss of each of the metals employed in the test are set out in Table 1:—

TABLE 1

Metal	Weight Loss in milligrams/square inch		
	Formulation A	Formulation B	Limits for Ford Test
Copper	115.5	0.1	2.0
Brass	6.67	0.1	2.0
Solder	2.0	1.7	4.0
Steel	0.4	0.3	2.0
Cast Aluminium	0.6	3.5	7.0
Cast Iron	1.5	1.4	2.0

- 15 These results demonstrate well the efficiency of an anti-freeze composition of the present invention in inhibiting the corrosion of metals, especially copper, compared with a similar anti-freeze composition.

EXAMPLE 2

20 The following aqueous acid cleaning composition was made up:—

- 74 parts by weight of water
15 parts by weight of 325-mesh diatomaceous earth abrasive
25 5 parts by weight of ethylene glycol
3 parts by weight of citric acid
2 parts by weight of 3 - amino - 1:2:4 - triazole
30 1 part by weight of thiourea

- A specimen of copper was polished with the acid cleaning composition. The cleaned specimen was then stored in an atmosphere with a relative humidity of 50% and at a temperature of 23° C. The first sign of tarnishing of the cleaned sample was observed after 6 weeks. A control copper sample showed signs of tarnishing after only one week.

EXAMPLE 3

- 40 The following aqueous isopropanol polish composition was made up:—

15 parts of α - alumina 325-mesh abrasive

84 parts of aqueous 20% isopropanol

1.0 part of 3 - amino - 1:2:4 - triazole 45

A bright copper specimen was polished with the polish and after applying the polish, the polish was allowed to dry to a residual powder which was then removed by light dusting.

The polished specimen was then stored in an atmosphere with a relative humidity of 50% and a temperature of 23° C. The first sign of tarnishing on the specimen occurred after six weeks whereas a control specimen of copper became tarnished after only one week. 55

EXAMPLE 4

A specimen of bright copper foil was immersed in the following solution:—

- (a) 1.0% weight/volume aqueous solution of 3 - amino - 1:2:4 - triazole having a pH value of 6.0 60

The immersed specimen was maintained at 60° C. for two minutes and then removed, washed with distilled water and dried in hot air. 65

The resistance to tarnishing of the copper specimen was compared with that of a control specimen, by exposing each of the specimens to an atmosphere containing 10 parts per million by weight of hydrogen sulphide. The time taken for the onset of visible tarnish was recorded and the results are set out in Table II:— 70

Specimen	Tarnish Time (minutes)
Control	1
Solution (a)	10

The results in Table II demonstrate the good protection afforded to copper by the compositions of the present invention.

EXAMPLE 5

The following solid mixture was made up:—

- (a) 80 parts by weight of pentasodium tri-
polyphosphate
19.6 parts by weight of sodium dodecyl-
benzene sulphonate
0.4 parts by weight of 3 - amino-
1:2:4 - triazole

A 0.5% weight/volume aqueous solution

was made up from the mixture (a) and the solution was then heated to 70° C. Articles of nickel silver cutlery were immersed in the solution and kept in the hot solution for a period of three hours.

At the end of this time nickel silver cutlery in the solution (a) was free from tarnishing but those in a control solution under the same conditions were heavily tarnished.

Bright copper specimens were heated in the respective solutions at 70° C. for 48 hours and the loss in weight of each copper specimen was observed at the end of this time. The results are summarised below:—

Specimen	Weight Loss (milligrams/square decimetres)
Immersed in control solution	37.0
Immersed in solution from (a)	5.0

EXAMPLE 6

A solid powder mixture was made which had the following composition by weight:—

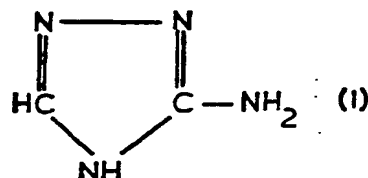
- 55 parts of citric acid
15 parts of thiourea
10 parts of sodium lauryl sulphate
20 parts of 3 - amino - 1:2:4 - triazole

A 10% weight/volume aqueous solution was made up from this powder and heated to 70° C. A bright copper specimen (1.5 inch square) was placed in the solution and left immersed for 5 minutes. At the end of this time, the specimen was washed, dried and exposed to an atmosphere containing 10 parts per million of hydrogen sulphide. The time taken for the onset of tarnish was 10 minutes which contrasts sharply with the time taken for the onset of tarnish on a control specimen, namely only 3 minutes.

Similar results were obtained when citric acid was replaced by the same amount of tartaric acid or sulphamic acid, the remaining conditions being the same.

WHAT WE CLAIM IS:—

1. A method of inhibiting the tarnishing of copper or alloys of copper comprising contacting the surface of the copper or alloy thereof with a solution containing 3 - amino-1:2:4 - triazole having the formula:—



2. A method as claimed in claim 1 wherein the sole solvent or the major component of the solvent system is water.

3. A method as claimed in claim 2 wherein the major component of the solvent system is water, the remainder being acetone or isopropanol.

4. A method as claimed in claim 3 wherein the proportion of 3 - amino - 1:2:4 - triazole is within the range of from 0.05% to 2.0% by weight.

5. A method as claimed in any of the preceding claims wherein the solution containing the 3 - amino - 1:2:4 - triazole is a polish base and comprises a mixture of water and alcohol.

6. A method as claimed in claim 5 wherein the polish base contains an abrasive.

7. A method as claimed in claim 6 wherein the abrasive is α -alumina red iron oxide or silica, finely divided so that at least 90% by weight of the abrasive material will pass

through a 325-mesh sieve. (B.S.S.)

8. A method as claimed in any of claims 1 to 5 wherein the solution containing the 3-amino - 1:2:4 - triazole is a polish base containing water as the sole solvent, an abrasive and one or more anionic or non-ionic surface active agents, the proportion of surface-active agent being within the range of from 5% to 30% by weight
9. A method as claimed in claim 8 wherein a proportion of a gelling agent within the range of from 0.5% to 5% by weight is also present in the polish base.
10. A method as claimed in any of claims 8 or 9 wherein the surface-active agent is an alkanolamine or alkali metal salt of a higher fatty acid or a condensation product of ethylene oxide with an alkyl phenol, a higher fatty acid or a higher fatty amine.
11. A method as claimed in claim 8 or claim 9 wherein the anionic surface-active agent is tri - ethanolamine- or sodium stearate, lauryl sulphate, sodium dodecyl benzene sulphonate or the condensation product of nine molar proportions of ethylene oxide with one molar proportion of nonyl phenol stearic acid or hexadecylamine respectively.
12. A method as claimed in any of claims 9 to 11 wherein a gelling agent which is methyl cellulose or polyvinyl pyrrolidone having a molecular weight in the region of 40,000 is present.
13. A method as claimed in any of claims 1 to 4 wherein the copper article is a small, non-decorative article and is contacted with the solution by dipping for a period of not more than five minutes.
14. A method as claimed in any of claims 1 to 4 wherein the solution containing the 3-amino - 1:2:4 - triazole is a detergent composition containing a sequestering agent for calcium and other polyvalent metal ions.
15. A method as claimed in claim 14 wherein the sequestering agent is tetra-sodium pyrophosphate, pentasodium tripolyphosphate, di-sodium dihydrogen pyrophosphate, pentapotassium tripolyphosphate, sodium or potassium metaphosphate, "hexasodium tetraphosphate" or "hexasodium hexametaphosphate".
16. A method as claimed in claim 14 or claim 15 wherein the detergent composition also contains an anionic surface-active agent having the formula:—



- wherein R represents an aliphatic hydrocarbon group and M represents an alkali metal or ammonium radical.
17. A method as claimed in claim 16 wherein the anionic surface-active agent is sodium myristyl sulphate, sodium hexadecyl sulphate potassium stearyl sulphate, ammonium oleyl sulphate, sodium lauryl sulphate, potassium lauryl sulphate, ammonium or sodium

stearyl sulphate, sodium oleyl sulphate, sodium or potassium 2 - ethylhexyl sulphate or sodium, potassium or ammonium lauryl alcohol sulphate.

18. A method as claimed in claim 14 or claim 15 wherein the detergent composition contains an anionic surface-active agent which is an alkali metal alkyl benzene sulphonate.

19. A method as claimed in claim 18 wherein the anionic surface-active agent is sodium dodecyl benzene sulphonate or sodium dodecyl naphthalene sulphonate.

20. A method as claimed in claims 16 to 19 wherein the proportion of the surface-active agent is within the range of from 10% to 30% by weight based on the total weight of the composition.

21. A method as claimed in any of claims 1 to 4 wherein the solution is a solution of an acidic cleaning composition comprising an acidic material having a pK value of not more than 5.0, thiourea and 3 - amino - 1:2:4-triazole.

22. A method as claimed in claim 21, wherein the acidic cleaning composition, in the form of a dry powder, is dissolved in water to give the desired concentration of each of the individual components of the acidic cleaning composition, and the copper surface is then immersed in this solution.

23. A method as claimed in claim 22 wherein the solution of the acidic cleaning composition is maintained at a temperature within the range of from 40° C. to 70° C.

24. A method as claimed in any of claims 21 to 23 wherein the 3 - amino - 1:2:4 - triazole is present in the acidic cleaning solution in a proportion within the range of from 0.1% to 10% by weight based on the total volume of the solution.

25. A method as claimed in any of claims 21 to 24 wherein the copper surface is immersed in the solution for a period within the range of from 30 seconds to 5 minutes.

26. A method as claimed in claims 21 to 25 wherein the acid cleaning solution containing an anionic surface-active agent as defined in any of claims 16 to 19.

27. A method as claimed in claim 26 wherein the proportion of surface-active agent is within the range of from 0.1% to 10% by weight based on the total weight of the composition.

28. A method as claimed in any of claims 1 to 4 wherein the solution containing the 3-amino - 1:2:4 - triazole is an antifreeze composition containing water and a water-miscible organic solvent.

29. A method as claimed in claim 28 wherein the organic solvent is ethylene glycol or glycerol.

30. A method as claimed in claim 28 or claim 29 wherein the proportion of 3 - amino-1:2:4 - triazole in the anti-freeze compo-

sition is within the range of from 0.01% to 5% by weight based on the total weight of the anti-freeze composition.

31. A method of inhibiting the tarnishing of copper or alloys of copper comprising contacting the surface of the copper or alloy thereof with an acidic cleaning composition comprising an acidic material having a pK value of not more than 5.0, thiourea and 3-amino - 1:2:4 - triazole in the form of an aqueous paste containing a mild abrasive material.

32. A method as claimed in claim 31 wherein the paste contains a water-miscible solvent.

33. A method as claimed in claim 32 wherein the water-miscible solvent is ethanol or iso-propanol.

34. A method as claimed in any of claims 31 to 33 wherein the proportion of 3 - amino-1:2:4 - triazole is within the range of from 10% to 40% by weight based on the total weight of the paste.

35. A method as claimed in any of claims 31 to 34 wherein the acidic cleaning composition contains an anionic surface-active agent as defined in any of claims 16 to 19.

36. A method as claimed in claim 35 wherein the proportion of surface-active agent is within the range of from 0.1% to 10% by weight based on the total weight of the composition.

37. A method of inhibiting the tarnishing of copper or alloys of copper comprising incorporating an acidic cleaning composition comprising an acidic material having a pK value of not more than 5.0, thiourea and 3 - amino-1:2:3 - triazole, into an inert carrier, moistening the carrier with water, and applying the

carrier to the copper or copper alloy surface to be treated. 40

38. A method as claimed in claim 37 wherein the inert carrier is a dry, high wet-strength paper carrier.

39. A method as claimed in claim 37 or claim 38 wherein the acidic cleansing composition is applied as a dry powder to the inert carrier, the proportion of 3 - amino - 1:2:4 - triazole being within the range of from 10% to 30% by weight based on the total weight of the dry composition. 45 50

40. A method of inhibiting the tarnishing of copper in accordance with Claim 1, substantially as described in any of the Examples.

41. A copper or copper alloy surface whenever treated by a method claimed in any of the preceding claims. 55

42. A composition for treating a copper or copper alloy surface comprising an aqueous alcoholic polish base, an aqueous detergent base, an aqueous acidic cleaner or anti-freeze base and 3 - amino - 1:2:4 - triazole. 60

43. An acidic cleaning composition comprising an acidic material having a pK value not more than 5, thiourea and 3 - amino-1:2:4 - triazole. 65

44. An acidic cleaning composition as claimed in claim 43 which is in the form of a dry solid mixture.

45. A composition for treating a copper or copper alloy surface in accordance with Claim 42 substantially as described in any of the Examples. 70

W. P. THOMPSON & CO.

Chartered Patent Agents,
Coopers Building, Church Street,
Liverpool 1.